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LEWIS ACID CATALYZED CYCLOADDITION REACTIONS OF 2,3-HOMOTROPONE WITH DIENES: [4π+2π] AND [3C(2π)+4π] CYCLOADDITIONS

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In the presence of Lewis acids, 2,3-homotropone 1 smoothly undergoes cycloaddition reactions with cyclopentadiene and butadiene in [4π+2π] fashion with "inverse electron demand," the dienes acting as dienophiles. With anthracene, however, 1 yields a [3C(2π)+4π] cycloadduct probably via 2-oxyhomotropylium cation.

The Diels-Alder reactions of α,β-unsaturated ketones and nitriles are markedly accelerated by Lewis acids owing to lowering the dienophiles LVMO energy.[1] In this sense, Lewis acids would facilitate a Diels-Alder reaction with "inverse electron demand"[2] between an α,β,γ,δ-unsaturated ketone and an electron rich olefin. In this regard, 2,3-homotropone 1 is an interesting system, because it contains a dienone moiety and isomerizes to 2-hydroxyhomotropylium cation in strongly acidic media.[3] It would therefore be expected that 1 behaves, under acidic conditions, as either an electron poor diene or an oxyhexatrienyl cation, with the latter [7C(6π)+4π] and [3C(2π)+4π] cycloadditions being possible. Reactions of 1 with usual dienophiles have been reported to yield normal Diels-Alder adducts.[4] We wish here to report that 1, under acidic conditions, undergoes cycloadditions with dienes in either [4π+2π] fashion with "inverse electron demand" or [3C(2π)+4π] fashion depending on the nature of dienes.

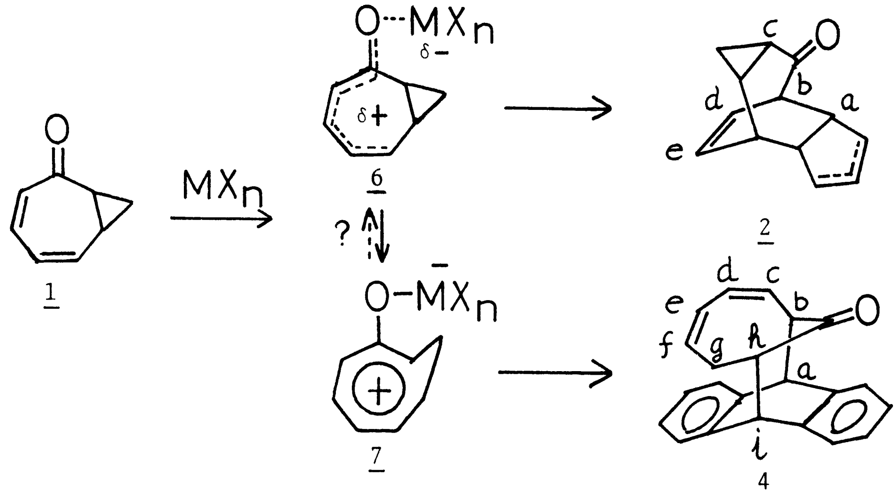
2,3-Homotropone 1 rapidly reacted with cyclopentadiene in the presence of $SnCl_4$ in dichloromethane at 0°C and gave the [4π+2π] adduct 2 in 81% yield after chromatography on SiO_2 [m.p. 60.5-61.5°C; $\nu_{C=O}$(KBr) 1680 cm^{-1}; δ ($CDCl_3$) 1.0 (2H, m), 1.5 (2H, m), 1.7-3.1 (6H, m), 5.5 (2H, m), 5.8 (2H, m)].[5] $BF_3 \cdot OEt_2$ and $AlCl_3$ also worked as the catalyst, although with the former the reaction was somewhat slower. The spectral data of 2 indicate the presence of a cyclopropyl ketone. For further structural elucidation, an $Eu(fod)_3$ (0.7 mol equiv) shifted spectrum was more informative. In this spectrum, five protons are clearly separated from the others at δ 4.38 (ddd, J=10, 6, 6 Hz, Hc), 4.88 (br. d, 8, Ha), 5.76 (slightly br. d, 6.5, Hb), 6.50 (t,∼7, He), and 6.83 (t,∼7, Hd), the assignment being confirmed by PMDR. The small $J_{a,b}$ ($\leqq$1 Hz) indicates the endo orientation of the cyclopentene.[6] The marked down-field shifts of Ha,b,c coincide with the assigned structure. The orientation of the cyclopropane is probably anti from steric point of view. The position of the double bond of the cyclopentene is, however, yet uncertain.

Under similar conditions, butadiene also readily added to 1 in a similar manner, giving a ca 4:5 (GLC) isomeric mixture of the adduct 3.[7]

However, with anthracene, a diene which hardly act as a dienophile, 1 slowly underwent cycloaddition in the presence of $SnCl_4$ at room temperature (one day) to give the [3C(2π)+4π] adduct 4 in 85% yield (SiO_2 chromatography) [m.p. 181-182°C; $\nu_{C=O}$(KBr) 1700 cm^{-1}; δ ($CDCl_3$) 1.3-2.3 (m, Hg,g'), 3.04 (dddd, J=12.2, 6.8, 6.8, 2.0 Hz, Hh), 3.58 (slightly br. d, 6.4, Hb), 4.12 (d, 6.8, Hi), 4.37 (d, 6.4, Ha), 5.58 (m, Hc-f), 7.25 (m, aromatic)]. The spectral data indicate the absence of a cyclopropane and are best interpreted as the assigned structure, the PMR signals being reasonably assigned as indicated above. In consistent with this structure, the signals of Hb and Hh were most largely down-shifted by $Eu(fod)_3$. Catalytic hydrogenation of 4 (5% Pd/C, EtOAc) afforded a tetrahydro-compound [m.p. 171-172°C; $\nu_{C=O}$(KBr) 1695 cm^{-1}; δ (CCl_4) 0.6-2.2 (10H, m), 2.80 (2H, m), 3.98 (2H, d, J=6.5 Hz), 7.18 (8H, m).], further supporting the structure of 4.

In the absence of the Lewis acids, 1 and cyclopentadiene slowly reacted at room temperature (one day) to yield 2 (42%) and the [2π+4π] adduct 5 [31%; m.p. 64-65°C; $\nu_{C=O}$(KBr) 1660 cm^{-1}; δ (CCl_4) 0.8-1.8 (6H, m), 3.0 (4H, m), 5.36 (1H, d, J=12.5 Hz), 5.7-6.4 (3H, m)]. The spectral data of 5 indicate the presence of a cyclopropane and an α,β-unsaturated ketone. Anthracene did not reacted even at 80°C.

The species reacting with cyclopentadiene and butadiene in the presence of the Lewis acids may be the Lewis acid coordinated 2,3-homotropone 6, whereas that with anthracene is probably the oxyhomotropylium cation 7.



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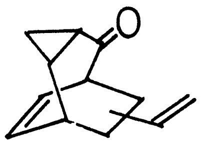

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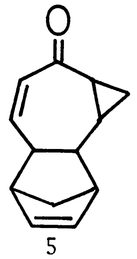

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5) Satisfactory elemental analyses or mass spectral data were obtained for all the new compounds in this paper.

6) For validity of the coupling constant for elucidation of the stereochemistrys in the related compounds see; S. Ito, K. Sakan, and Y. Fujise, Tetrahedron Lett., 775 (1969); 2873 (1970).

7) The adducts could be separated by SiO_2 column chromatography. The spectra of both the adducts resemble each other, and indicate the presence of a cyclopropane and a vinyl group. Further structural elucidations are undergoing.

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